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14. ABSTRACT
This contract targeted mathematical and computational underpinnings of a predictive capability for high performance, nano-composite materials. The overall goal is to develop theory, models, and numerical algorithms for the processing pipeline, starting with composite information, through flow processing, and finally to multi-functional property characterization. The materials considered are nano-rods and nano-clays in acqueous and polymeric solvents, which are flight technology targets for high performance properties ranging from electrical, thermal, mechanical, and permeability. Significant progress has occurred in the theory and models for flow processing and effective properties, in the analysis, numerical algorithms and simulations of the models, and in scientific understanding of nano-composite materials.

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HIGH PERFORMANCE MACROMOLECULAR MATERIALS

AFOSR F49620-03-1-0098
Final Project Report
June 5, 2006

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Abstract This project targets mathematical and computational underpinnings of a predictive capability for high performance, nano-composite materials. The overall goal is to develop theory, models, and numerical algorithms for the processing pipeline, starting with composite information, through flow processing, and finally to multi-functional property characterization. The materials we consider are nano-rods and nano-clays in acqueous and polymeric solvents, which are technology targets for high performance properties ranging from electrical, thermal, mechanical, and permeability. We have made progress in the theory and models for flow processing and effective properties, in the analysis, numerical algorithms and simulations of the models, and in scientific understanding of nano-composite materials.

The theoretical basis for flow processing of nano-composites is the nematic or polymeric liquid crystal theory of Doi, Hess, Marrucci and Greco. The theory applies to nano-scale rods and platelets (macromolecules) in viscous solvents. (Forest and Wang have published extensions of the theory and models to include polymeric solvents during this contract period.) Extensions to flexible and more geometrically complex elements are challenging, and under study. Post-processing predictions to infer multi-functional properties is based on homogenization theory, where the information from flow processing fits directly into the homogenization results for effective property tensors. We have predicted effective thermal, electrical, permeability, and mechanical property tensors, with only electrical properties published so far, in collaboration with Rob Lipton, LSU. Results on mechanical properties were submitted just this month.

During and as a consequence of flow processing, the nano-particle ensemble is theoretically described in terms of an orientational probability distribution function (PDF). In extension-dominated flow, such as fiber processing, features of the PDF have been shown by the authors in previous contracts to be predictable and controllable. In film and mold-filling processing, anomalous dynamical responses of the nano-ensemble and generation of spatial gradient morphology have been the subject of intense experimental, theoretical and computational scrutiny for the past two decades. The theory has simply not been available to make predictions of relevance to technology, and in particular, the mathematical community has only recently engaged these challenges. Forest and collaborators have made significant progress on a controlled understanding of model experiments in which the flow is shear-dominated, representative of film and mold processing. We have further made significant advances in mapping flow-induced PDFs of the nano-ensemble to effective properties.

Specifically, we build theory, models, and simulations that provide the link from control parameters: composition (viscous solution or polymer matrix plus nano-elements), processing flow type and rates, and confinement conditions (device lengthscales as well as solid boundaries); to multi-functional material properties.

A significant obstruction in the production pipeline is control over anisotropy and heterogeneity of performance properties in nano-composites, which arise on lengthscales between the molecular and device scales. These property features are clearly a consequence of the orientational morphology of the anisotropic nano-inclusions, which are typically long rod-like or thin platelet molecules with aspect ratios between 20 and 2000. At present, these anisotropic ensembles and spatial morphologies of the nano-inclusions, and subsequently of the effective properties of materials, are viewed as problematic. However, these features are only possible in soft matter materials, and offer potential keys to novel materials. We currently have theory, modeling, and simulation predictions with a host of the relevant chemical composition and processing physics built in. Other physics and chemistry are not on solid theoretical foundation yet, such as non-uniform mixing of the nano-elements and a polymeric solvent rather than a viscous liquid, and we have made some progress in incorporating them into the framework.

In our approach, the design and control pipeline is divided into a sequence of fundamental theory and computation problems:

- Molecular potentials and process controls determine the micron-scale, physical structures due to molecular orientational distributions generated in films and molds, as well as stored elastic stresses in these viscoelastic composites. The mathematical theory and models, analytical solution methods, and numerical simulation tools for these orientational anisotropy and structure properties and associated stored stresses are the central components of our research over the past three years.

- Once the micron-scale molecular morphology is characterized, either as a numerical database, analytical scaling properties, or an experimentally determined dataset, the next challenge to mathematics and computation is the determination of effective material performance properties. Since there are millions of molecules in a cubic micron, clearly one must develop scale-up methods based on the molecular orientational distribution, molecule properties, the solvent or matrix properties, and the geometry of the material (film thickness, mold shape). Here we have teamed with Robert Lipton, Louisiana State University, to marry the results of composite homogenization theory with our molecular structure morphology results. This gives the effective anisotropic composite property tensor, parametrized by composition and processing parameters.

- The last stage in the pipeline is a direct solve for the performance features of the film, using the mechanical, thermal, electric, piezoelectric, permeability property tensor(s) of the nano-composite, which are the variable, anisotropic coefficients in an elliptic, second- or fourth-order operator, together with realistic boundary conditions the materials are exposed to during performance conditions. We have only begun to run simulations for this purpose.

- Finally, a control wrapper is necessary that measures performance properties, evaluates them based on a cost functional which penalizes departure from desired properties, and then gives feedback to which composition and processing parameters can minimize cost and thereby achieve desirable performance features. This capability is realistic within the next 5 years.

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Eric Choate	Graduate student, UNC (to graduate, December, 2006)
Xiaoyu Zheng	Graduate student, UNC (graduated May, 2006)
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Publications since 2004

1. The weak shear kinetic phase diagram for nematic polymers, (with Q. Wang, R. Zhou), Rheologica Acta, Volume 43, Number 1, 17-37 (2004).

2. Internal Constraint Theories for the Thermal Expansion of Viscous Fluids, (with S.E. Bechtel, F.J. Rooney), International Journal of Engineering Science, Vol. 42, 43-64 (2004).

3. Structure scaling properties of confined nematic polymers in plane Couette cells: the weak flow limit, (with Q. Wang, H. Zhou, R. Zhou), J. Rheology, Volume 48(1), 175-192, January/February (2004).

4. Scaling behavior of kinetic orientational distributions for dilute nematic polymers in weak shear, (with Q. Wang, R. Zhou), JNNFM Volume 116, Issue 2-3, 183-204 (2004).

5. A kinetic theory for solutions of nonhomogeneous nematic liquid crystalline polymers with density variations, (with Q. Wang, R. Zhou), Journal of Fluids

Engineering, Volume 126, 180-188 (2004).

6. Monodomain response of arbitrary aspect ratio nematic polymers in general linear planar flows, (with Q. Wang, R. Zhou, E. Choate), JNNFM, Volume 118(1), 17-31 (2004).

7. Kinetic theories and mesoscopic models for solutions of nonhomogeneous liquid crystal polymers, (with C. Calderer, Q. Wang), JNNFM, Volume 120(1), 69-78 (2004).

8. Likelihood & expected-time statistics of monodomain attractors in sheared discotic and rod-like nematic polymers, (with Zheng, X., Zhou, R., Wang, Q.), Rheol. Acta, Volume 43(1), 17-37 (2004).

9. The flow-phase diagram of Doi theory for sheared nematic polymers, II: finite shear rates, (with Zhou, R., Wang, Q.), Rheol. Acta, Vol. 44(1), 80-93 (2004).

10. Chaotic boundaries of nematic polymers in mixed shear and extensional flows, (with R. Zhou, Q. Wang), Physical Review Letters, Volume 93(8), 088301, August (2004).

11. Exact scaling laws for electrical conductivity properties of nematic polymer nano-composite monodomains, (with X. Zheng, R. Lipton, R. Zhou, Q. Wang), Advanced Functional Materials, Volume 15(4), 627-638, April (2005).

12. Kinetic structure simulations of nematic polymers in plane Couette cells, I: The algorithm and benchmarks, (with R. Zhou, Q. Wang), SIAM Multiscale Modeling and Simulation, Volume 3(4), 853-870 (2005).

13. Extension-enhanced conductivity of liquid crystalline polymer nano-composites, (with H. Zhou, X. Zheng, Q. Wang, R. Lipton), Macromolecular Symposia, Volume 28, 81-85 (2005).

14. A numerical study of unsteady, thermal, glass fiber drawing processes, (with H. Zhou), Communications in Mathematical Sciences, Volume 3(1), 27-45 (2005).

15. Connections between stability, convexity of internal energy, and the second law for compressible Newtonian fluids, (with S.E. Bechtel, F. Rooney, and Q. Wang), ASME J. Applied Mechanics, (2005).

16. Anisotropy and dynamic ranges in effective properties of sheared nematic polymer nano-composites, (with X. Zheng, R. Zhou, Q. Wang, R. Lipton), Advanced Functional Materials, Vol. 15, 2029-2035 (2005).

17. Hydrodynamic theories for mixtures of polymers and rodlike liquid crystalline polymers, (with Q. Wang), Physical Review E, Volume 72, 041805: 1-17 (2005).

18. Anisotropy and heterogeneity of nematic polymer nano-composite film properties, (with R. Zhou, Q. Wang, X. Zheng, R. Lipton), Institute for Mathematics and Its Applications, Volume 141, **Modeling of Soft Matter**, 85-98 (2005).

19. A new proof on uniaxial equilibria of a 3-dimensional Smoluchowski equation, (with H. Zhou, H. Wang, and Q. Wang), Nonlinearity, Volume 18, 2815-2825 (2005).

20. Kinetic structure simulations of nematic polymers in plane Couette cells, II: In-plane structure transitions, (with R. Zhou, Q. Wang), SIAM Multiscale Modeling and Simulation, Volume 4(4), 1280-1304 (2005).

21. Alignment and rheo-oscillator criteria for sheared nematic polymer films in the monolayer limit, (with J. Lee, R. Zhou), Discrete and Continuous Dynamical Systems, Volume 6, 339-356 (2006).

22. Anchoring distortions coupled with plane Couette & Poiseuille flows of nematic polymers in viscous solvents: morphology in molecular orientation, stress & flow, Discrete and Continuous Dynamical Systems, Volume 6, 407-425 (2006).

23. On weak plane Couette and Poiseuille flows of rigid rod and platelet ensembles, (with Z. Cui, Q. Wang, H. Zhou), SIAM J. Applied Math, Vol. 66, Number 4, 1227-1260 (2006).

24. A classical problem revisited: Rheology of nematic polymer monodomains in small amplitude oscillatory shear, (with E. Choate), Rheologica Acta, ISSN: 0035-4511 (Paper) 1435-1528 (Online), March, (2006).

25. Nematic liquids in weak capillary Poiseuille flow: structure scaling laws and effective conductivity implications, (with H. Zhou), Int. J. Numerical Analysis & Modeling, to appear (2006).

26. Nano-rod suspension flows: a 2D Smoluchowski-Navier-Stokes solver, (with R. Zhou, Q. Wang), Int. J. Numerical Analysis & Modeling, to appear (2006).

Submitted refereed research articles and web-posted preprints

27. Spatial coherence, rheological chaotic dynamics, and hydrodynamic feedback of nematic polymers in plate-driven shear, (with R. Zhou, Q. Wang), Phys. Rev. Lett., submitted July, 2005, in revision.

28. Anchoring-induced structure transitions of flowing nematic polymers in plane Couette cells, (with H. Zhou, Q. Wang), JNNFM, to be submitted, 2006.

29. A correspondence principle between Stokes flows of viscous and viscoelastic fluids, (with I. Klapper, K. Xu), JNNFM, submitted, April, 2006.

30. Monodomain dynamics for rigid rod & platelet suspensions in strongly coupled coplanar linear flow and magnetic fields, (with Q. Wang, R. Zhou), J. Rheology, submitted, February, 2006.

31. Characterization of stable kinetic equilibria of rigid, dipolar rod ensembles for coupled dipole-dipole and excluded-volume potentials, (with H. Zhou, H. Wang, Q. Wang), Nonlinearity, submitted, January, 2006.

32. Autoregressive & maximum likelihood methods for microrheological characterization of viscoelastic media, (with J. Fricks, L. Yao, T. Elston), J. Rheology, to be submitted, 2006.

33. Extension of the Ferry shear wave model for viscoelastic characterization to finite depth, wave reflection, and nonlinearity, (with S. Mitran, B. Lindley, L. Yao), JNNFM, to be submitted, 2006.

34. Nematic polymer mechanics: flow-induced anisotropy, (with X. Zheng, R. Lipton, R. Zhou), Continuum Mechanics & Thermodynamics, submitted June 2, 2006.

Honors & Awards Received

Grant Dahlstrom Distinguised Professor of Mathematics, UNC, effective July1, 2004

AFRL Point of Contact

Richard Vaia, AFRL/MLBP, Bldg 654, WPAFB, OH, Phone 937-255-9184. Met at American Chemical Society meeting, where Forest gave an invited talk in the Polymer Nano-composites Symposium, co-organized by Vaia, March 15, 2005, San Diego, CA.